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A request for examination in accordance with § 44, German Patent Law, has been filed.

54. Exhaust Gas Purification Catalyst for Use with Internal Combustion Engines and Process for its Production

Abstract:

The invention relates to an exhaust gas purification catalyst (6, 7) for use in internal combustion engines. The exhaust gas purification catalyst (6, 7) consists of a porous, monolithic substrate (10), a catalyst layer (11, 12) which is formed on the surface of the monolithic substrate (10) and contains a catalytic material which is capable of purifying the exhaust gases, in which case the catalyst layer (11, 12) contains, at a location close to the exhaust gas output end of the monolithic substrate (10), a palladium-carrying layer (13). Palladium is distributed in high concentration in this palladium-carrying layer (13).

[See graph on page 1 of the German source document.]

Conventional Catalyst

Vertical (y-axis):
HC Light-off Temperature

Horizontal (x-axis):
Thickness of the Palladium-Carrying Layer

Description

Background and Environment of the Invention

The present invention relates, in general, to an exhaust gas purification catalyst for use in internal combustion engines and, in particular to an exhaust gas purification catalyst which consists of a porous monolithic substrate and of a catalyst layer applied to the surface of said monolithic substrate. Furthermore, the present invention relates to a process for the production of such an exhaust gas purification catalyst.

Prior Art

Some of the conventional, and known, exhaust gas purification catalysts consist of a porous, monolithic substrate which consists of cordierite or a similar material formed on the surface of the monolithic substrate. The catalyst layer contains catalytic materials to promote the oxidation of hydrocarbons (HC), carbon monoxide (CO) or the like, and the reduction of nitrogen oxides (NO_x) contained in the exhaust gases. Generally used catalytic materials are those which contain precious metal components or other metal components, for example, platinum, rhodium or the like (hereinafter these materials will be referred to as catalytic precious metals). In the case of these conventional exhaust gas purification catalysts, the catalytic precious metals are essentially evenly distributed. However, the temperature and exhaust gas velocity fluctuate from one point to the next within the exhaust gas purification catalysts while the exhaust gas purification ratio of the catalytic precious metals is a function of the catalyst's temperature and of the gas's velocity. Therefore, conventional exhaust gas purification catalysts, in which the catalytic precious metals are distributed evenly, cannot sufficiently increase the exhaust gas purification ratio.

Laid open Japanese Patent Application No. 61-46 252 discloses an exhaust gas purification device, in which the distribution of the concentration of the catalytic precious metals fluctuates in accordance with the temperature distribution or the gas velocity within the exhaust gas purification catalyst.

Fig. 1 shows the design of such an exhaust gas purification device which essentially consists of a cylindrical housing 102 communicating with an exhaust line 101, and in which case housing 102 contains a exhaust gas purification catalyst 103. Exhaust gas purification catalyst 103 consists of a monolithic substrate and a catalyst layer which contains catalytic precious metals and is formed on the surface of said monolithic substrate. This catalyst 103 is divided into three segments 104, 105 and 106, whereby the first segment 104 contains a high concentration of catalytic precious metals, and the second and third segments 105, 106 contain a low concentration of catalytic precious metals. The third segment 106 has an essentially constant width and is arranged upstream of the other two segments 104 and 105 when viewed in the direction of flow of the exhaust gas. The first segment 104 is adjacent to the third segment 106 and

comprises a longitudinal section extending along the longitudinal axis of catalyst 103 so that the longitudinal cross-section has the form of a "T." The third segment 105 extends around the longitudinal section of the first segment 104.

However, if the engine is cold and the temperature of the exhaust gas is correspondingly low, exhaust gas purification catalyst 103 in the device of Fig. 1 exhibits only a low catalytic effect so that the purification ratio of the exhaust gases is very low. In addition, the temperature values close to the longitudinal axis are generally higher than in the peripheral segments. Inasmuch as, in the case of a conventional catalyst, the concentration of the catalytic precious metals is high in the region close to the longitudinal axis of the catalytic converter, the temperature becomes particularly high at this location, which causes the catalytic precious metals, in particular platinum, to sinter together. As a result, exhaust gas purification catalyst 103 may be destroyed by heat.

The present invention has been developed in order to avoid the aforementioned disadvantages.

Consequently, this invention is to solve the problem of providing an exhaust gas purification catalyst for use in internal combustion engines, said exhaust gas purification catalyst being capable of increasing the ratio of exhaust gas purification by increasing the efficiency of the catalytic converter when the engine is cold and exhaust gas temperature values are low; in addition, this catalyst should feature a simple design and low manufacturing costs.

In order to solve this problem, the exhaust gas purification catalyst of the present invention consists of a porous, monolithic substrate, a catalyst layer which is formed on the surface of the monolithic substrate and contains the catalytic material which is capable of purifying exhaust gases, and of a palladium-carrying layer which is provided in the catalyst layer at a location close to the exhaust gas input end of the monolithic substrate. Palladium is distributed in high concentrations in this palladium-carrying layer.

Inasmuch as the palladium-carrying layer having a high palladium concentration, which, in turn, significantly promotes the oxidation reaction, is provided in accordance with the present invention close to the exhaust gas input end of the exhaust gas purification catalyst, the oxidation of hydrocarbons or similar harmful substances contained in the palladium-carrying layer is increased considerably so that, in this manner, a large amount of heat is developed. It is for this reason that the temperature of the exhaust gases in the palladium-carrying layer is increased. High-temperature exhaust gases pass through the section of the catalyst located downstream of the palladium-carrying layer and the temperature is increased also in this section, thereby increasing the efficiency of the entire exhaust gas purification catalyst. This results in the increased efficiency of the catalyst at lower temperatures and in an improved exhaust gas purification ratio.

Even though the temperature of the catalyst in the palladium-carrying layer becomes high, there is no sintering because palladium is highly resistant to heat. In this manner, a thermal destruction of the catalyst can be effectively prevented.

In accordance with another aspect of the present invention, an exhaust gas purification device consists of an exhaust manifold, a first converter located downstream of the manifold, said converter containing a catalyst for performing a preliminary treatment of the exhaust gases, and of a second converter located downstream of the first converter, which said second converter contains the above-described catalytic exhaust gas purification catalyst.

Yet another aspect of the present invention relates to a process for the production of the above-described exhaust gas purification catalyst; in this case, a first layer of aluminum is first applied to the porous, monolithic substrate, then a second layer of cerium oxide is applied to said first layer. Thereafter, a palladium-carrying layer is formed in the second layer at a location close to the exhaust input end of the monolithic substrate.

With reference to the attached drawings, the following description shows examples of embodiment which illustrate the essence of the invention even more clearly. The same reference numbers are used for the same parts in the drawings. They show:

Fig. 1 a longitudinal section of a conventional exhaust gas purification device;

Fig. 2 a schematic longitudinal section of an exhaust gas purification device provided with a catalyst for exhaust gas purification in conjunction with the present invention;

Fig. 3 a cross-section of a first or a second catalyst in accordance with the present invention;

Fig. 4 a longitudinal section of a first or second catalyst;

Fig. 5 a flow diagram illustrating the manufacturing processes used for the first or the second catalyst;

Fig. 6 a schematic longitudinal section of a water-absorbent material and a monolithic substrate material arranged in an impregnating receptacle;

Fig. 7 a perspective illustration of an exhaust gas purification catalyst which has a palladium-carrying layer on its inside surface;

Fig. 8 a graph which shows the relationship between the light-off temperature of the hydrocarbons and the thickness of the palladium-carrying layer of the different catalysts;

Fig. 9 a graph similar to that of Fig. 8, which shows the values of Fig. 8 after the catalysts of Fig. 8 have been exposed to air having a temperature of 900°C for a period of 50 hours;

Figs. 10 through 12 show schematic views of patterns of common catalysts which have been provided for comparison with the catalysts of the present invention; and

Fig. 13 a schematic partial view of the usual pattern of a catalyst of Fig. 12.

Fig. 2 of the drawings shows an exhaust gas purification device for internal combustion engines which consists of an exhaust manifold 1, of an essentially cylindrical primary catalytic converter 3 which is located downstream of exhaust manifold 1 and connected with said exhaust manifold via an exhaust line 2, and of an essentially cylindrical main catalytic converter 5 which is located downstream of primary catalytic converter 3, in which case said main catalytic converter 5 is also connected with converter 3 via an exhaust line 2. Primary catalytic converter 3 accommodates an essentially column-shaped catalyst 4 for the preliminary treatment of the exhaust gas. Main catalytic converter 5 converts hydrocarbons (HC), carbon monoxides (CO), or similar gases contained in the exhaust gas into carbon dioxide and water, and also converts nitrogen oxides (NO_x) into nitrogen. Main catalytic converter 5 accommodates essentially column-shaped first and second exhaust gas purification catalysts 6 and 7 to promote oxidation and reduction, and an essentially column-shaped oxidation catalyst 8 to promote oxidation only, in which case each of these catalysts is arranged in the disclosed sequence in the direction of the exhaust gas flow.

As shown in Fig. 3, the first exhaust gas purification catalyst is a monolithic catalyst and consists of a monolithic substrate 10 having a honeycomb design with a large number of small holes 9 extending in longitudinal direction and of a catalyst layer 11 formed on monolithic substrate 10, as well as a second catalyst layer 12 formed on first layer 11. The catalyst components making up the first catalyst layer 11 are aluminum as the main component, and a platinum component (hereinafter simply referred to as platinum), as well as a rhodium component (hereinafter simply referred to as rhodium), as catalyst components, while the components making up the second catalyst layer 12 are cerium oxide (C_5O_2) as the main component, as well as a palladium component (hereinafter simply referred to as palladium), whereby both components form the catalyst component. A process for the production of catalyst layers 11 and 12 will be described later.

As shown in Fig. 4, in the case of the second catalyst layer 12 of the first exhaust gas purification catalyst 6, palladium is distributed in high concentration close to the exhaust input, in which case a palladium-carrying layer 13 is formed. Contrasted with this, the second catalyst layer 12 located downstream of palladium-carrying layer 13 no longer contains any palladium, so that, in this manner, a layer 14 without palladium is formed.

It should be noted that the second exhaust gas purification catalyst has a design similar to the first catalyst 6.

A process for the production of the first exhaust gas purification catalyst will now be described in conjunction with Fig. 2 through 4 and the flow diagram of Fig. 5.

(1) Process Step P1

First, 540 g of gamma-aluminum (gamma Al_2O_3), 60 g of boehmite and 1 liter of water are mixed and then 10 ml of nitric acid are added in order to create a suspension for the first catalyst layer 11. The desired amount of suspension can be achieved by increasing or decreasing the quantity of each material that is to be used, whereby, however, the mixing ratio should be constant.

(2) Process Step P2

Monolithic substrate 10 is immersed in the suspension. Monolithic substrate 10 consists of a cordierite cylinder which has a diameter of 25.4 mm and a length of 50.8 mm. The number of small holes 9 extending in longitudinal direction of monolithic substrate 10 is approximately 62 per cm^2 cross-section.

(3) Process Step P3

The monolithic substrate is removed from the suspension and placed in an air stream in order to remove excess suspension from the substrate.

(4) Process Step P4

Monolithic substrate 10 which has been exposed to the stream of air is dried at 250°C for approximately two hours.

(5) Process Step P5

Dried monolithic substrate 10 is heated for two hours to 650°C so that the first catalyst layer 11 is formed on the surface of monolithic substrate 10. In the case of the above-described process steps P2 through P5, the first catalyst layer 11 has been adjusted to 14 % by weight with respect to monolithic substrate 10.

(6) Process Step P6

A solution of a platinum chloride is prepared in appropriate concentration, and a solution of rhodium chloride is prepared in appropriate concentration.

(7) Process Step P7

Monolithic substrate 10, to which the first catalyst layer 11 has already been applied, is immersed in the platinum chloride solution and, thereafter, in the rhodium chloride solution, so that the platinum and the rhodium are carried by the first catalyst layer 11. The quantity of platinum and rhodium in the first catalyst layer 11 totals 1.6 g/L, and the concentration of both solutions, as well as the immersion time, are adjusted in such a manner that a ratio of platinum to rhodium of 1:5 is achieved.

(8) Process Step P8

Monolithic substrate 10 which carries the platinum and the rhodium is dried.

(9) Process Step P9

Monolithic substrate 10 is heated in such a manner that the platinum and the rhodium are fixed in the first catalyst layer 11.

(10) Process Step P10

The second catalyst layer 12 is then formed on the first catalyst layer 11 of monolithic substrate 10. The process for forming the second catalyst layer 12 is similar to the process used for the first catalyst layer 11 (process steps P1 through P5), with the exception that the components of the suspension are different. The suspension for the second catalyst layer 12 is prepared in that 540 g of cerium oxide (C_eO_2), 60 g of boehmite and 1 liter of water are mixed and that, thereafter, 10 ml of nitric acid are added. The desired amount of suspension may be achieved, of course, in that the quantities of the individual materials are increased or decreased, whereby, however, the above mixing ratio must be kept constant. In this process step P10, the second catalyst layer 12 is adjusted to 28 % by weight relative to the monolithic substrate 10.

(11) Process Step P11

A solution of palladium chloride is prepared in an appropriate concentration.

(12) Process Step P12

As illustrated by Fig. 6, a water-absorbent material 16, for example, a sponge, a piece of cloth or the like is placed in an impregnating receptacle and caused to absorb a solution of palladium chloride. Water-absorbent material 16 is molded in this manner such that it is capable of good contact with one surface of monolithic substrate 10.

(13) Process Step P13

As shown by Fig. 6, monolithic substrate 10, on which the first and second catalyst layers 11 and 12 are formed, is applied to the water-absorbent material in such a manner that the surface of monolithic substrate 10 on the input side of the exhaust gases is in contact with the upper surface of water-absorbent material 16. Then, monolithic substrate 10 is pressed against water-absorbent material 16 for a specific period of time so that the palladium of second catalyst layer 12 is deposited on the exhaust gas input side surface of monolithic substrate 10. In this case, the concentration of the palladium chloride solution and the pressure applied to monolithic substrate 10 are adjusted in such a manner that a palladium-carrying layer 13 will have a thickness of 5 mm in longitudinal direction of monolithic substrate 10 and the amount of applied palladium (the concentration of distributed palladium) will be 0.5 g/L.

This process for forming palladium-carrying layer 13 on a monolithic substrate 10 with the use of a water-absorbent material 16 can be used to achieve, in a highly accurate manner, a desired value of the thickness of the palladium-carrying layer in longitudinal direction of monolithic substrate 10 and, in addition, can be used to considerably reduce the loss of palladium chloride solution. Moreover, a palladium-carrying layer 13 having a desired cross-section may be formed on one surface of monolithic substrate 10 by varying the size of the contact surface between the water-absorbent material and monolithic substrate 10. As shown, for example in Fig. 7, a palladium-carrying layer 19 can be applied to the internal surface of an exhaust gas purification catalyst only in the vicinity of one of said catalyst's internal end surfaces.

Usually, such a palladium-carrying layer is formed in that a specific length of a monolithic substrate is immersed in a palladium chloride solution in an impregnating container, or in that the palladium chloride solution is sprayed on the end surface of the monolithic substrate.

However, the first-mentioned process is not advantageous because the palladium-carrying layer cannot be formed only in one section close to the end surface of catalyst 18 and because the concentration of the palladium chloride solution must be changed in order to control the thickness of the palladium-carrying layer.

On the other hand, the latter process is disadvantageous because the palladium-carrying layer cannot be formed only in one section close to the end surface of the catalyst and because the thickness of the palladium-carrying layer cannot be properly adjusted; furthermore, the loss of palladium chloride solution is considerable.

(14) Process Step P14

Monolithic substrate 10 which has already been coated with the second palladium-carrying catalyst layer 12 is dried at 250°C for a period of 2 hours.

(15) Process Step P15

Monolithic substrate 10 is heated in such a manner that the palladium of second catalyst layer 12 is fixed.

Fig. 8 is a graph which shows the result of the measured temperatures at which the ratio of hydrocarbon purification of the exhaust gas purification catalyst is 50%. Hereinafter, this temperature will be referred to as light-off temperature for hydrocarbons (HC Light-Off Temperature [sic]), this temperature being a measure of the efficacy of catalysts at low temperatures. If the light-off temperature for hydrocarbons becomes low, the efficacy of catalysts at lower temperatures is increased. Samples of exhaust gas purification catalysts 6 were produced essentially following the aforementioned production process, in which case, however, the amount of palladium applied to the palladium-carrying layer 13 was changed within the range of 0.1 g/L to 1.0 g/L, and in which case, furthermore, the thickness of the palladium-carrying layer in longitudinal direction of the monolithic substrate was changed within the range of 2 mm to 15 mm.

Furthermore, the graph of Fig. 8 shows the light-off temperature for hydrocarbons of an exhaust gas purification catalyst which was produced in accordance with the conventional method described hereinafter:

(a) The first catalyst layer is formed by using a method similar to that used for process steps P1 to P9 of Fig. 5.
(b) A solution of palladium chloride is added and mixed with cerium oxide (C_eO_2) powder, and then dried. Following the reduction to small pieces, a cerium oxide powder is prepared, which carries the palladium, or contains the palladium fixed in it.
(c) 540 g of cerium oxide powder with the palladium incorporated, 60 g of boehmite and 1 liter of water are mixed, and subsequently 10 ml of nitric acid are added, thereby producing a suspension.
(d) A monolithic support which has already been coated with a first catalyst layer is immersed in the suspension, dried and heated, thus forming the second catalyst layer. In this case, the second catalyst layer is adjusted to 28% by weight with respect to the monolithic substrate, and the amount of palladium is a uniform 1.0 g/L.

Fig. 9 shows a graph illustrating the result of the measurement of the light-off temperature for hydrocarbons which was obtained after the above-described exhaust gas purification catalysts had been exposed for 50 hours to air having a temperature of 900°C.

As is clearly obvious from Fig. 8 and 9, the enhancement effect of the efficacy at lower temperature is minimal when the amount of applied palladium is lower than 0.35 g/L. If the amount of applied palladium exceeds 1.0 g/L, the effect of increased activity at lower temperature is almost at its maximum. Therefore, the amount of applied palladium is suitably selected within the range of 0.35 g/L to 1.0 g/L, and preferably within the range of 0.5 g/L to 1.0 g/L. It makes sense to select the thickness (extension in longitudinal direction) of the palladium-carrying layer within the range of 2 mm to 7 mm, preferably within the range of 2 mm to 5 mm, because it is difficult to adjust the thickness of the palladium-carrying layer to a value of less than 2 mm with high accuracy by using these manufacturing processes and because a layer having a thickness (extension) greater than 7 mm offers only a minimal effect when the activity is increased at lower temperatures.

For comparison with the above-described example of embodiment, Table 1 shows the result of a measurement of efficacy at lower temperatures and the purification ratio with reference to three types of example catalysts which have been produced essentially in accordance with the conventional method. The measuring process will be described later.

(1) Example Catalyst 1

As shown by Fig. 10, the individual catalyst layer containing aluminum as the basic component is formed on a monolithic, column-shaped substrate having a diameter of 25.4 mm and a height of 50 mm. The catalyst layer consists of two A-layers, each having a relatively low catalyst concentration, and of a B-layer having a relatively high catalyst concentration. These three layers are arranged successively — starting at the exhaust gas input side — in longitudinal direction of the monolithic substrate in such a manner that first there is an A-layer (7 mm) and then the B-layer (10 mm) and then another a A-layer (33 mm). In precious metal catalysts, the composition of the A-layer and the B-layer is as follows:

A-layer:
Pt: 0.25 g /1178 ml
Pd: 0.25 g /1178 ml
Rh: 0.05 g /117 ml
Pt/Pd/Rh = 4.5 / 4.5 / 1.0
Precious metal content of catalyst: 0.46 g/L

B-layer:

Pt: 0.5 g /1178 ml

Pd: 0.5 g /1178 ml

Rh: 0.1 g /1178 ml

Pt/Pd/Rh = 4.5 / 4.5 / 1.0

Precious metal content of catalyst: 0.92 g/L

(2) Example Catalyst 2

As shown by Fig. 11, a column-shaped monolithic substrate having a diameter of 25.4 mm and a height of 50 mm is coated with a single catalyst layer which contains aluminum as its basic component. A B-layer (7 mm) and an A-layer (43 mm) are applied in this sequence — starting at the exhaust gas input side — in longitudinal direction of the monolithic substrate. The composition of the precious metal catalyst of the A-layer and the B-layer is analogous to that of Example 1.

(3) Example Catalyst 3

As shown by Fig. 12 and 13, a dual catalyst layer consisting of a first layer (C_3), which contains aluminum as its basic component, and of a second catalyst layer (C_1+C_2), which contains cerium oxide as its basic material. This dual layer is formed on a column-shaped monolithic substrate having a diameter of 25.4 mm and a height of 50 mm. The C_3-layer is applied to the monolithic substrate, and the C_1-layer is applied to the C_3-layer from the exhaust gas input end to a point at a distance of 2 mm from said end, viewed in longitudinal direction of the monolithic substrate. The C_2-layer, which has a width of 48 mm, is arranged on the C_3-layer at the exhaust gas output side, namely, adjacent to the C_1-layer. The composition of the precious metal catalyst in the A-layer and in the B-layer is as follows:

The C_1-layer does not contain any precious metal catalyst component.

C_1-layer:

Pt/Pd/Rh = 4.5 / 4.5 / 1.0

Precious metal content of catalyst: 0.5 g/L

C3-layer:

Pt/Rh = 5.0 / 1.0

Precious metal content of catalyst: 0.9 g/L

Following this, the efficacy of the catalysts at low temperatures is rated based on the light-off temperature at which 50% of the hydrocarbon, the carbon monoxide, or the nitrogen oxide contained in the exhaust gases can be converted at an air/fuel ratio of 14.7. As has already been described, the efficacy at a higher temperature is greater whenever the light-off temperature is lower. The above measurement was taken after each of the example catalysts had been stored for 50 hours in air having a temperature of 900°C.

Table 1

	Exhaust Gas Components					
	HC		CO		NO_x	
	Test					
	I (°C)	II (%)	I (°C)	II (%)	I (°C)	II (%)
Example Catalyst 1	320	82	290	69	298	71
Example Catalyst 2	300	88	305	72	280	78
Example Catalyst 3	280	96	255	80	240	81

Note:

Test 1: Light-off temperature (efficacy at low temperature).

Test II: Purification ratio (this ratio denotes the reduction ratio of HC, CO of NOx if the input temperature of the exhaust gas has been set at 400°C.

As is shown by Table 1, the light-off temperature in the case of each of the three Example Catalysts 1 through 3 which have been produced in accordance with a conventional method is generally high, and, consequently, the efficacy at lower temperature is low. Furthermore, the purification ratio of the exhaust gases is low.

For example, Example Catalyst 3 exhibits a hydrocarbon light-off temperature of 280°C, which is lower than that of any of the other example catalysts. However, each of the catalysts of Fig. 9 in accordance with the present invention exhibits light-off temperatures for hydrocarbon of less than 220°C, and the lowest light-off temperature for hydrocarbon is approximately 200°C. In view of these facts, it has been found that the efficacy of the catalysts of the present invention is considerably higher at lower temperatures than the efficacy of catalysts which have been produced in accordance with the conventional method.

Although the B-layer (7 mm) of Example Catalyst 2 exhibiting a high catalyst concentration is formed in the vicinity of the exhaust gas input end, an efficacy-increasing effect at low temperatures is hardly noticeable. From this fact it can be learned that the enhancement effect of an efficacy at a lower temperature cannot generally be achieved by increasing the catalyst concentration on the exhaust gas input side. In other words, the effect of increased efficacy at lower temperatures can be achieved only if the

palladium concentration on the exhaust gas input side is increased, as is true of the catalysts of the present invention.

Although Example Catalyst 3 comprises a dual-layer catalyst layer as in the aforementioned example of embodiment of the present invention, the effect of enhancing the efficacy at lower temperatures is very minimal. Consequently, the efficacy at lower temperatures cannot generally be increased by configuring the catalyst layer as a dual-layer layer. Therefore, it has been known that superior efficacy at low temperatures can be achieved by forming a zone of high palladium concentration at the exhaust gas input end and, at the same time, by applying a dual-layer layer in this zone.

Although, in this example of embodiment, the section (layer 14 without palladium) — different from palladium-carrying layer 13 — does not contain palladium, palladium may be distributed in low concentration over the entire second catalyst layer, and a high-concentration palladium-carrying layer may be formed in the vicinity of the exhaust gas output end.

In addition, a single catalyst layer containing cerium oxide (C_eO_2) as its main component, as well as platinum and rhodium as catalyst components, may be prepared without forming two catalyst layers. In this case, a palladium-carrying layer is formed in that palladium is carried by a catalyst layer at a point close to the exhaust gas input end.

Although the present invention has been described in detail with the use of examples and with reference to the attached drawings, it should be noted that various changes and modifications made by one skilled in the art are possible. Therefore, unless such changes and modifications deviate from the spirit and scope of the present invention, they are to be considered as being covered by the scope of this invention.

Patent Claims

1. Exhaust gas purification catalyst (6, 7) for use with internal combustion engines, **characterized by** a porous monolithic substrate (10),
a catalyst layer (11, 12) which is formed on the surface of the monolithic substrate (10) and contains a catalytic material which is capable of purifying exhaust gases, and
a palladium-carrying layer (13) which is formed in the catalyst layer (11, 12) at a location close to the exhaust gas output end of the monolithic substrate (10), in which case a high concentration of the catalytic material of the palladium is distributed in the palladium-carrying layer (13).

2. Catalyst (6, 7) in accordance with Claim 1, characterized in that the catalyst layer (11, 12) contains platinum and rhodium as additional catalyst components.

3. Catalyst (6, 7) in accordance with Claim 2, characterized in that a zone, different from the palladium-carrying layer (13), does not contain palladium.

4. Catalyst (6, 7) in accordance with Claim 2, characterized that a zone, different from the palladium-carrying layer (13), also contains palladium, but in a lower concentration than the palladium-carrying layer (13).

5. Catalyst (6, 7) in accordance with Claim 2, characterized in that the catalyst layer (11, 12) consists of a first layer (11) of aluminum, said layer containing the platinum and the rhodium, and consists of a second layer (12) applied to the first layer (11), said second layer consisting of cerium oxide, in which case the palladium-carrying layer (13) is formed in the second layer (12).

6. Exhaust gas purification device for use in internal combustion engines, characterized by an exhaust manifold (1),
a first converter (3) which is located downstream of the exhaust manifold (1) and communicates with said manifold, in which case said converter (3) contains a catalyst (4) for performing a preliminary treatment of the exhaust gases, and
a second converter (5) which is located downstream of the first converter (3) and communicates with said first converter, in which case said second converter (5) contains at least one exhaust gas purification catalyst (6, 7) which, in turn, consists of the following components:
a porous monolithic substrate (10),
a catalyst layer (11, 12) which is formed on one surface of the monolithic substrate (10) and contains a catalytic material which is suitable for the purification of the exhaust gases, and
a palladium-carrying layer (13) which is formed in the catalyst layer (11, 12) at a location close to the exhaust gas input end of the monolithic substrate (10), in which case the palladium is distributed in high concentration in the catalytic material of the palladium-carrying layer (13).

7. Device in accordance with Claim 6, characterized in that the catalyst layer (11, 12) also contains platinum and rhodium as catalyst components.

8. Device in accordance with Claim 7, characterized in that a zone, different from the palladium-carrying layer (13), does not contain palladium.

9. Device in accordance with Claim 7, characterized in that a zone, different from the palladium-carrying layer (13), also contains palladium, but in a lower concentration than the palladium-carrying layer (13).

10. Device in accordance with Claim 7, characterized in that the catalyst layer (11, 12) consists of a first layer (11) of aluminum which contains platinum and rhodium, and of a second layer (12) of cerium oxide, said second layer being formed on the first layer (11), and in which case the palladium-carrying layer (13) is formed in the second layer (12).

11. Process for the manufacture of an exhaust gas purification catalyst (6, 7) for use in an internal combustion engine, characterized by the following process steps:
production of a porous monolithic substrate (10),
formation of a first layer (11) of aluminum on the monolithic substrate (10),
formation of a second layer (12) of cerium oxide on the first layer (11), and
formation of a palladium-carrying layer (13) in the second layer (12) at a location close to the exhaust gas output end of the monolithic substrate (10), in which case catalytic material of palladium is distributed in high concentration in the palladium-carrying layer (13).

12. Process in accordance with Claim 11, characterized in that the first layer (11) contains platinum and rhodium.

Regarding this, see 5 pages of drawings.

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Fig. 1 (Prior Art)
[See German source text.]

Fig. 2
[See German source text.]

Fig. 3
[See German source text.]

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Fig. 4

Exhaust gas input side [See German source text.] Exhaust gas output side

Fig. 6

[See German source text.]

Fig. 7

[See German source text.]

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Fig. 5
[See flow-diagram in German source text.]

P1 Prepare suspension	P9 Heat
P2 Immerse substrate	P10 Prepare second layer
P3 Place substrate in stream of air	P11 Prepare palladium solution
P4 Dry	P12 Absorption of palladium-solution in water-absorbent material
P5 Heat	P13 Introduce catalyst in water-absorbent material
P6 Prepare precious metals	P14 Dry
P7 Immerse substrate	P15 Heat
P8 Dry	

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Fig. 8
[See graph in German source text.]

Conventional Catalyst

y-axis: HC light-off temperature
x-axis: Thickness of the palladium-carrying layer

Fig. 9
[See graph in German source text.]

Conventional Catalyst

y-axis: HC light-off temperature
x-axis: Thickness of the palladium-carrying layer

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Fig. 10 *Fig. 11*
[See graphs in German source text.]

Unit: mm Unit: mm

Fig. 12 *Fig. 13*
[See graphs in German source text.]

Unit: mm